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Monte-Carlo Simulation of Polarization-Selective Spectral Hole Burning
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Theoretical and numerical simulations of spectral hole burning in fractal clusters are carried out. Selective photofragmentation of fractals induced by powerful laser radiation is considered, as observed in silver clusters in colloidal solutions and gels.

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MONTE-CARLO SIMULATION OF POLARIZATION-SELECTIVE SPECTRAL HOLE BURNING IN FRACTAL CLUSTERS

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INTRODUCTION

Fractals, objects of noninteger dimensionality embedded into usual (three dimensional) space, possess many nontrivial mathematical properties [1,2]. There exists a series of physical systems whose geometry can be adequately described as fractal [3-5]. We shall restrict ourselves to the study of one of such physical realizations of fractals. namely fractal clusters [5] (simply called below as fractals). More specifically, we shall consider theoretically the selective photomodification of fractals induced by powerful laser radiation. Experimentally, this phenomenon has recently been observed [6] in silver clusters in colloidal solutions and gels.

The effect of selective photomodification observed in Ref. [6] consists in burning out the spectral hole in the absorption contour of a fractal at the frequency close to that of the exciting laser radiation. The spectral hole exists at times on the order of months or longer and, thus, can be considered as persistent. The primary hole is highly dichroic: it is observed only in the polarization of the probe light coinciding with that of the exciting radiation and is practically absent for the normal polarizations. In solutions this dichroism relaxes with the rotational diffusion times of the clusters. and in gels it does not significantly change for months. The experimental data [6] indicate that the photomodification has a threshold in the intensity of the laser radiation. Below we shall exploit the last feature to develop the theory of the photomodification which should explain its selectivity and give further predictions to stimulate experimental study.

THEORY AND NUMERICAL SIMULATION OF SPECTRAL HOLE BURNING IN FRACTALS

The fractal is modelled as the set of N polarizable particles, called monomers, located at the points r_i, $i = 1.....N$. The total size of the fractal R_c is assumed to be much less that the incident light wavelength λ. Therefore the electric field $\mathbf{E}^{0)}$ of the light wave can be considered to be the same at the sites of all the monomers. The external plus local electric field (i.e.. the integral field of all the other monomers) induce on the ith monomer a transition dipole moment d_i oscillating with the light frequency, which obeys the well-known system of equations

$$d_{i\alpha} = \chi_0 E_\alpha^{(0)} - \chi_0 \sum_{j=1}^{N}{}' \left[\delta_{\alpha\beta} - 3n_\alpha^{(ij)}n_\beta^{(ij)} \right] r_{ij}^{-3} d_{j\beta} \ . \tag{1}$$

where the Greek subscripts stand for tensor components (summation over repeated indices is implied), and the Latin indices stand for ordinal numbers of monomers; χ_0 is the dipolar polarizability of an individual (isolated) monomer: $r_{ij} = r_i - r_j$; and $n^{(ij)} = r_{ij}/r_{ij}$.

The properties of the monomer enter the system (1) only via the polarizability χ_0. Taking this into account. we shall consider as the spectral variable not the light

frequency ω, but the quantity $X \equiv \mathrm{Re}\chi_0^{-1}$. As the characteristic of the dissipation in the monomer, we shall use the parameter $\delta \equiv \mathrm{Im}\chi_0^{-1}$. To make the connection to experiment, let us specify the relation between X and ω in a model which is realistic, in particular, for clusters obtained by aggregation in colloidal solutions. This model considers the monomer as a macroscopic sphere with radius R_m, consisting of the material with a complex dielectric permittivity $\varepsilon \equiv \varepsilon' - i\varepsilon''$. The polarizability of such a sphere is given by the well-known expression $\chi_0 = R_m^3(\varepsilon - 1)(\varepsilon - 2)^{-1}$. For the metallic sphere, the permittivity is well described by the Drude formula $\varepsilon = \varepsilon_0 - \omega_p^2/[\omega(\omega - i\gamma)]^{-1}$, where $\varepsilon_0=$const is the contribution of the interband transitions (e.g., for silver $\varepsilon_0 \approx 5$), ω_p is the electron plasma frequency, and γ is the electron collision frequency. For most metals, in particular, for the noble metals, $\gamma \ll \omega_p$ and, consequently, $\varepsilon'' \ll \varepsilon'$. In this case, from (7) and (25), one can see that $X(\omega)$ turns to zero at the point of the surface plasmon resonance, $\omega = \omega_s$, where $\varepsilon' = -2$. From (26) it follows that $\omega_s \approx \omega_p(\varepsilon_0 + 2)^{-1/2}$. In the vicinity of the surface plasmon resonance, X and δ are simply expressed in terms of the detuning from the resonance $\Omega = \omega - \omega_s$, and the transition dipole moment of the resonance $|d_{12}|^2 = 3R_m^3\hbar\omega_p/[2(\varepsilon_0 + 2)^{3/2}]$, namely $X = \hbar\Omega/|d_{12}|^2$, $\delta = \hbar\gamma/2|d_{12}|^2$.

The theory is based on the above mentioned assumption of the threshold character of the photomodification. In addition it is assumed that the photomodification is local, i.e. only those monomers are modified for which the amplitude of the local field E_i exceeds the threshold magnitude E_{th}. The latter depends on the composition of the monomer and the embedding medium, and also on the specific mechanism of the photomodification. Note that the local field is simply expressed through the solution of Eq. (1), $\mathbf{E}_i = \mathbf{d}_i/\chi_0$. For the sake of definiteness, we also suppose that the modified monomers do not contribute to the optical absorption. This assumption is suggested by the estimates [6] that the modification mechanism, apparently, consists of melting and evaporation of the monomer material.

The numerical study has been carried out in the following way. Three types of fractals are generated and used in the simulation: random walks (the fractal dimension $D = 2$), self-avoiding random walks ($D \approx 1.7$) and Witten-Sander clusters ($D \approx 2.5$), where the number of clusters of each type is 1000, with mean number of the monomers in the cluster as $\bar{N} = 50$. The results obtained for all the three fractal types are quite similar, so that we shall give all the numerical illustrations only for the random-walk fractals.

For each individual fractal, the basic system of equations (1) is solved numerically and the factor G_i of enhancement of the local field for the ith monomer is found, $G_i = |\mathbf{E}_i|^2/(\mathbf{E}^{(0)})^2$. The above-discussed condition of modification is taken in the form

$$G_i \geq G_{th}, \quad G_{th} \equiv \left(E_{th}/E^{(0)}\right)^2. \tag{2}$$

Those monomers for which this condition is met are excluded from the fractal. After that, the system (1) is solved once again for the modified fractals (with the excluded monomers). The optical absorption A per one monomer is determined from the formula $A = \mathrm{Im}\chi_{zz}$, where $\chi_{zz} = \langle d_z\rangle/E^{(0)}$, and the polarization of the exciting wave is, for the sake of definiteness, directed along the z-axis. Note that the absorption cross-section σ_a per one monomer is related to A by $\sigma_a = 4\pi A/3$. It can be shown that the number ΔN of the modified (excluded) monomers is expressed as $\Delta N = \int_{-\infty}^{\infty} \Delta A(X)\mathrm{d}X$, where ΔA is the change of absorption upon the photomodification.

In Ref. [7] we have found the estimate G of the mean of G_i over the ensemble of fractals in the scaling region ($\delta \ll |X| \ll R_0^{-3}$) as

$$G \equiv \langle G_i\rangle \sim Q(R_0^3|X|)^{d_0+1}. \tag{3}$$

where R_0 is the characteristic separation between the nearest monomers in the fractal. $d_o \approx 0.4$ is the optical spectral dimension. and $Q = (R_0^3 \delta)^{-1}$ is the quality factor of the resonance in the monomer. For many monomer materials. including the noble metals. the Q-factor is large: e.g.. for silver. $Q = 3 - 30$ depending on the defect concentration in the metal determined by the preparation method. Thus. the factor G is large. which means that fluctuations of the local field are much grater than the exciting field $E^{(0)}$. This fact. in the light of Eq. (2). allows us to predict that the photomodification takes place at high values of $G_{th} \sim G$. In the other words. the characteristic light intensity of photomodification of fractals is much smaller (by the factor $\sim G^{-1} \ll 1$) than the threshold intensity of the isolated monomer modification. This is a consequence of large fluctuations of local fields in the nontrivial fractals and. also. of the high Q-factor of the monomer resonance (cf. Eqs. (2) and (3)).

In Fig. 1 we present an example of the dependence of the relative number of modified (removed) monomers $\Delta N/N$ on the threshold parameter G_{th}, with the value X^* of the X-parameter for the modifying radiation as $X^* = 3.0$. One can see that. in accord with the above arguments. the photomodification starts at large values of G_{th}. which correspond to small exciting field intensity $E^{(0)2}$.
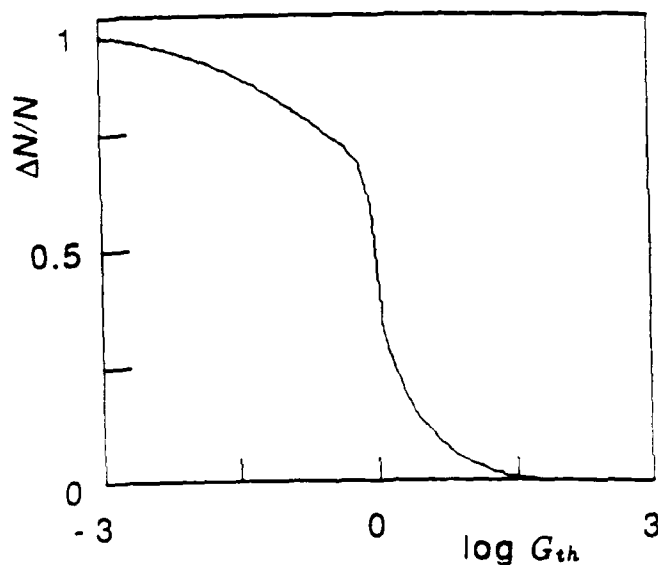

Fig. 1. The relative amount of the modified monomers as the function of the threshold parameter G_{th} (2) calculated for $Q = 3$.

An example of the calculated fractal absorption contour is shown in Fig. 2. One can see that this contour is a broad peak centered at the zero X, corresponding to the frequencies near the surface-plasmon resonance. The differential spectrum of the photoburning, i.e.. the difference between the fractal absorption before and after the modification. is shown in Fig. 3 for the two polarizations of the probing field and $X^* = -1$. It follows from this figure that for the parallel polarization the spectral hole is burned out. centered at the frequency of the exciting radiation ($X \approx X^*$). For the perpendicular polarization. the spectral hole at $X \approx X^*$ practically disappears, while it emerged at the "mirror" frequency at $X \approx -X^*/2$. This can be understood in the framework of the binary approximation developed in Ref. 8. Thus. in fact, the spectral hole is highly dichroic. As the numerical results show. in accord with the theoretical estimates and Figs. 1 and 2. the width of the hole burned (in the X-variable) is on order of Q^{-1}. while the total width of the fractal contour is on order of unity independently of the Q-parameter. Thus. the total number of holes. which can be burned out in each of the two polarizations. can be estimated as approximately $2Q$.
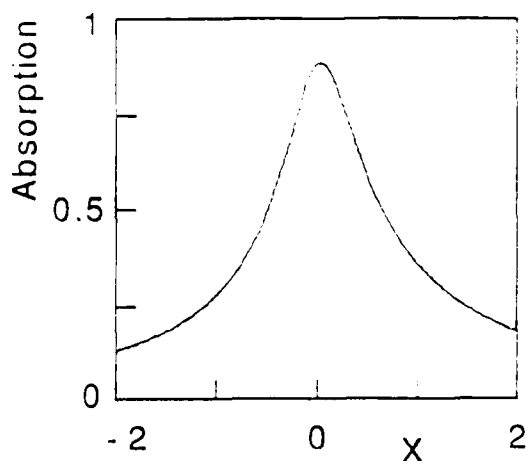
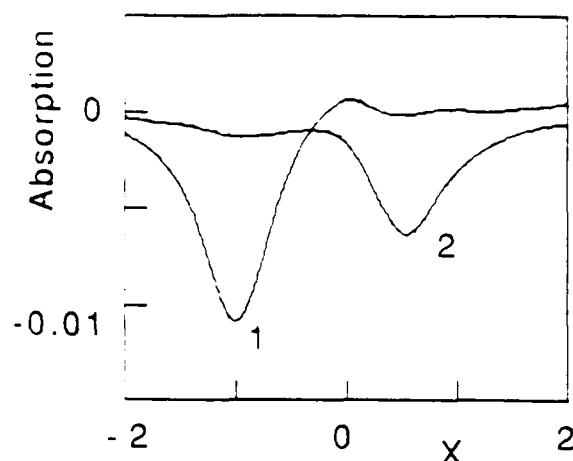Fig. 2. Absorption spectrum of the clusters calculated for $Q = 3$

Fig. 3. Difference in the absorption spectrum caused by the photomodification calculated for $Q = 3$, $X^* = -1$, with the polarization parallel (curve 1) and perpendicular (curve 2) to that of the modifying radiation

CONCLUDING DISCUSSION

The theory presented above describes a qualitative picture of the polarization-selective persistent spectral-holes photoburning in fractals, which has been experimentally observed [6]. The estimate obtained on the basis of the numerical results shows that it is possible to burn out in a given spatial region of a fractal media the number of $\approx 2Q$ frequency- and polarization-resolvable spectral holes. This number may be on order of 10 for the realistic value of $Q = 1 - 10$. Thus, the fractal cluster media are promising materials for high-density optical recording of information.

ACKNOWLEDGMENTS

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